

Synthesis and characterization of film-forming poly(urethaneimide) cationomers containing quaternary ammonium groups

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Abstract

In a recent work, we have described an original family of poly(urethaneimides) containing tertiary amine groups from a polytetramethylene oxide diol (PTMO1000), *N*-methyldiethanolamine (MDEA), 4,4'-methylene-bis-phenylisocyanate (MDI) and 4,4'-hexafluoroisopropylidene-bis-phthalic anhydride (6FDA). This paper reports their quaternization with various alkylating agents to give the cationic quaternary ammonium groups. An optimization of the experimental conditions led to three new families of PUI cationomers with a good structural control and high quaternization degrees. These polymers differed in the number of their cationic groups ($0 < x \leq 0.7$ equiv.), the type of their counter-ions X^- (methyl sulfate, tosylate, triflate, chloride, bromide, iodide) and their steric hindrance by the length of their *n*-alkyl side chain (C_1 – C_6). Complementary NMR techniques, including HSQC and COSY two-dimensional NMR, enabled to characterize the control of the polymer structure and to determine quantitatively the quaternization degree of the PUI cationomers. Properties in solution (solubility and viscosity) and in the solid state (film-forming ability and density) were then examined in relation with the membrane separation application targeted for these new PUI cationomers.

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1. Introduction

Poly(urethaneimide) block copolymers are film-forming materials with interesting features for membrane separation processes. Their really high withstanding to solvent exposure and the possibility to vary their permeability and selectivity make them particularly suitable for separating organic mixtures by pervaporation and vapor permeation [1,2]. Most often, their chemical structure can also be varied gradually with interesting prospects for fundamental studies to identify original structure–property relationships [3–5].

In a preceding work, we have obtained an original family of poly(urethaneimides) (PUI/*x*) containing tertiary amine groups in their polymer backbone from the *N*-methyldiethanolamine (MDEA) reactant [6]. The new synthesis method led to the

PUI copolymers in high yields, with a good structural control and in particular that of their tertiary amine content *x*. The quaternization of the tertiary amine groups of these PUI copolymers with various alkylating agents can lead to different types of quaternary ammonium groups. These PUI copolymers are thus reactive polymers which can be considered as versatile precursors for the synthesis of a wide range of poly(urethaneimide) cationomers.

A few other works have already shown the excellent performances of ammonium-containing polymers for the purification of the methyl-*tert*-butyl ether (MTBE) and ethyl-*tert*-butyl ether (ETBE) fuel octane enhancers [7–9]. However, the rather poor control of their macromolecular structure did not allow any detailed analysis of the role of the cationic groups on their selective permeability.

In this work, the quaternization of the PUI precursors leads to several families of PUI cationomers which differ in the number *x* of their cationic groups, the nature of their counter-ions

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X^- and their steric hindrance through the control of the length of their *n*-alkyl side chain R.

One of the great advantages of this new approach is that it is possible, from the same batch of PUI precursor, to obtain several PUI cationomers with the same macromolecular backbone, which thus only differ in the characteristics related to their ammonium groups. The properties of these cationomers can then be easily compared to those of the corresponding precursor, which gives the specific influence of the cationic sites in a straightforward way. Another advantage is the great structural variety allowed by this synthesis scheme which should open the way for the first systematic fundamental analysis of the influence of cationic groups on the selective permeability of cationomers towards purely organic mixtures of industrial interest.

This new approach to original PUI cationomers containing ammonium groups has been briefly explored in a short communication reporting preliminary results for a given family of polymers [10]. To the best of our knowledge, this short communication followed the single former paper in the literature on the synthesis of PUI cationomers containing ammonium groups reported by Al-Salah [11] and proposed a new synthesis scheme with both a gain of one step compared to the former route and great structure variability.

Nevertheless, a further investigation has since then shown that the quaternization step can be sometimes fairly difficult to handle. In particular, the main challenge is to operate in optimal conditions, i.e. soft enough to avoid deteriorating polymer chemical functions while still providing high quaternization degrees. Therefore, the synthesis of several families of new PUI cationomers with a strict structural control required another thorough investigation which is the subject for this paper.

In a first part, we describe the synthesis of three new families of PUI cationomers, the soft conditions required for the successful chemical modification of the corresponding PUI precursors and the solving of the particular problem of introducing long *n*-alkyl side chains which had not been properly identified at the early stage of our first preliminary study. Various spectroscopic techniques including two-dimensional NMR enabled to characterize the control over the polymer structure and the ammonium content for each polymer of the new families.

The second part focuses on some general features of the PUI cationomers. A few properties in solution (solubility and viscosity) and in the solid state (film-forming ability and density) are eventually discussed in relation to the membrane applications targeted for these new polymers.

2. Experimental section

2.1. Materials

1-Propanol (99.5+% Aldrich), 1-butanol (99.5% Merck), 1-pentanol (puriss. p.a. Fluka), 1-hexanol (99% Fluka), dichloromethane (99% Aldrich), chloroform (99% Carlo Erba) and petroleum ether ($T_{eb} = 35-60$ °C Carlo Erba) were stored for one week over molecular sieves 4 Å under argon before use.

The polytetramethylene oxide diol (PTMO1000, Merck) was used as received. 4,4'-Methylene-bis-phenylisocyanate (MDI, TCI) was distilled under vacuum and stored at -20 °C. *N*-Methyldiethanolamine (MDEA, Aldrich) was fractionally distilled under vacuum and stored over 4 Å molecular sieves. 4,4'-Hexafluoroisopropylidene-bis-phthalic anhydride (6FDA, Lancaster) was sublimed twice under reduced pressure. In order to prevent contamination by atmospheric moisture, all the former reagents were stored under dry argon.

Methyl *p*-toluenesulfonate (methyl tosylate MeOTs, 97% Acros), methyl trifluoromethanesulfonate (methyl triflate MeOTf, 99+% Aldrich), ethyl trifluoromethanesulfonate (ethyl triflate EtOTf, 99% Aldrich), trifluoromethanesulfonic anhydride (triflic anhydride, 98+% Acros), bromomethane (99.5+% Aldrich), 1-bromoethane (99% Fluka), 1-bromo-*n*-propane (98% Aldrich), 1-bromo-*n*-butane (97% Aldrich), 1-bromo-*n*-pentane (97% Aldrich), 1-bromo-*n*-hexane (98% Aldrich), chloromethane (99.5+% Aldrich) and iodomethane (99% Aldrich) were used without further purification.

Pyridine (99.5% Aldrich) was distilled over sodium hydroxide and stored over 4 Å molecular sieves under dry argon. Dimethyl sulfate (99% Aldrich) was distilled under reduced pressure (ca. 1 mm Hg) and stored at 6 °C under dry argon. *N,N*-Dimethylformamide (DMF, pure for synthesis, SDS) was distilled fractionally over calcium hydride under reduced pressure (ca. 5 mm Hg) and stored over 4 Å molecular sieves.

2.2. Synthesis

2.2.1. Alkyl trifluoromethanesulfonates (alkyl triflates ROTf)

n-Propyl, *n*-butyl, *n*-pentyl and *n*-hexyl triflate were prepared by adapting a literature procedure reported by Fife et al. [12]. A solution of the corresponding ROH primary alcohol (3 mmol) and pyridine (1 equiv., 0.25 mL) in 3 mL CH_2Cl_2 was added dropwise at 0 °C under vigorous stirring to a solution of triflic anhydride (1.1 equiv., 0.56 mL) in 3 mL CH_2Cl_2 under dry argon and left to react for an additional 45 min at the same temperature. The pyridinium salt by-product was eliminated by filtration-chromatography of the reaction mixture on a short column (diameter 6 mm, length 10 mm) of aluminium oxide (neutral aluminium oxide 90, activity 1, Merck) and dichloromethane was then removed under reduced pressure at room temperature. The crude product was extracted into dry petroleum ether and then filtered to eliminate the last traces of pyridinium triflate. The pure alkyl triflates were recovered by carefully removing the solvent in vacuum at room temperature and stored under argon at -20 °C. Yields: 65–70%. The 1H NMR spectra ($CDCl_3$) confirmed the purity of the C_3 to C_6 triflates thus prepared and were in good agreement with the literature data [12–14].

2.2.2. Poly(urethaneimide) precursors (PUI x)

The synthesis of the precursors PUI x (i.e. (PTMO1000 (1 – x equiv.) + MDEA (x equiv.)/MDI (2 equiv.)/6FDA (1 equiv.)) containing x equiv. ($x = 0.2-0.7$) of MDEA tertiary amine groups was formerly reported [6]. In the present work, the former procedure — which had been initially

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